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Effects of densified silica fume on microstructure and compressive strength of blended cement pastes

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Abstract

Some experimental investigations on the microstructure and compressive strength development of silica fume blended cement pastes are presented in this paper. The silica fume replacement varies from 0% to 20% by weight and the water/binder ratio (w/b) is 0.4. The pore structure by mercury intrusion porosimetry (MIP), the micromorphology by scanning electron microscopy (SEM) and the compressive strength at 3, 7, 14, 28, 56 and 90 days have been studied. The test results indicate that the improvements on both microstructure and mechanical properties of hardened cement pastes by silica fume replacement are not effective due to the agglomeration of silica fume particles. The unreacted silica fume remained in cement pastes, the threshold diameter was not reduced and the increase in compressive strength was insignificant up to 28 days. It is suggested that the proper measures should be taken to disperse silica fume agglomeration to make it more effective on improving the properties of materials.

Keywords: Silica fume; Agglomeration; Microstructure; Compressive strength

1. Introduction

Silica fume is a by-product of the manufacture of silicon or of various silicon alloys [1]. Silica fume, which contains more than 80–85% SiO_2 in amorphous form, is suitable to use in the cement and concrete industries [2]. The typical particle size of silica fume is around 0.1–0.5 μm and the nitrogen BET surface is 20,000 m^2/kg [3]. It is being used increasingly in the world as a mineral admixture to produce high-performance concrete (HPC) [12].

Silica fume is light and has a low bulk density, which may cause difficulty in transporting and handling. Commercial suppliers have responded by processing silica fume using different methods of densification and compaction in order to improve the handling and transport properties of material, such as densified, slurried or pelletized to increase its bulk density [4].

In previous papers, some researchers pointed out that there is high degree of agglomeration of silica fume in cement pastes or mortars [4–6,8,9]. The silica fume in its densified state considerably decreases its chemical reactivity with calcium hydroxide. The unreacted core of silica fume agglomeration was found by EDXA analyses at a long curing age of 1 year. The agglomeration of silica fume particles cannot be easily broken up due to the high interparticle forces, for example, forces due to electrostatic charging, Van der Waal's forces and forces due to moisture. This agglomeration of silica fume can easily reduce its effectiveness on properties of cement paste and mortar, because of the existence of densified grains of silica fume, which have a larger diameter, a smaller specific surface area (SSA) and a lower pozzolanic reactivity than the unitary grains. Many researchers showed that silica fume is highly reactive [1,2,17], while some papers reported the slow pozzolanic reaction of silica fume [6,15]. This fact may be caused by silica fume particle size rather than chemical composition (typically of high SiO_2 content). In this paper, experimental investigation was carried out to study the effects of densified silica fume on microstructure and compressive strength development of blended cement pastes. The objective of this paper is to indicate that the total dispersion of densified silica fume is of great importance, or the loss of performances of the blended cement pastes on both microstructure and mechanical property may happen.

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2. Experimental investigation

2.1. Raw materials

Ordinary Portland cement (OPC) and commercial condensed silica fume (CSF) were used as raw materials. The chemical composition and physical properties of OPC and CSF are listed in Table 1. The particle size distributions of ordinary Portland cement and silica fume by laser diffraction are shown in Fig. 1. It is clear from Fig. 1 that the size of silica fume agglomerates is much coarser than cement particles; many silica fume agglomerates have sizes larger than 100 μm although silica fume has a high nitrogen BET SSA. The reason for this high BET SSA is that nitrogen can penetrate into the space of original silica fume particles inside the agglomeration. Thus, the laser diffraction measures the agglomeration size while nitrogen measures the original size.

2.2. Sample preparation

Silica fume blended cement pastes CSF5, CSF10, CSF15 and CSF20 (which denoted blended pastes of water/binder ratio (w/b) = 0.4 and 5%, 10%, 15% and 20% (by weight) silica fume replacement, respectively) were prepared for tests. The OPC paste (CSF0) was prepared with water/cement ratio (w/c) = 0.4 as a control. The raw materials were mixed in a mortar mixer for 3 min and casted into steel cube moulds (50 × 50 × 50 mm), then compacted by tamping rod. The samples were sealed by plastic sheet to prevent water evaporation. They were removed from the moulds after 24 h and then cured in water at 20 ± 1 °C during 3, 7, 14, 28, 56 and 90 days of curing time.

2.3. Scanning electron microscopy (SEM) test

The particle characteristics of silica fume and the morphologies of the hydration products were measured by SEM. The samples were dried in vacuum desiccator and then investigated by SEM. At certain curing ages, OPC paste CSF0 and silica fume blended paste CSF5, CSF10, CSF15 and CSF20 were crushed and treated with acetone to stop the hydration, and then further dried in vacuum desiccator. The fresh broken faces were studied by SEM.

Table 1
Properties of raw materials

Properties	OPC	CSF
Oxide composition (wt.%)		
CaO	62.8	3.68
SiO_2	21.6	85.49
Al_2O_3	5.5	0.13
Fe_2O_3	3.5	0.45
SO_3	2.2	0.05
MgO	1.3	1.55
K_2O	0.53	0.19
Na_2O	0.05	0.23
Loss on ignition (%)	1.0	3.02
Blaine fineness (m^2/kg)	345	–
BET SSA (m^2/g)	–	25.06
Density (kg/m^3)	3.1	2.3

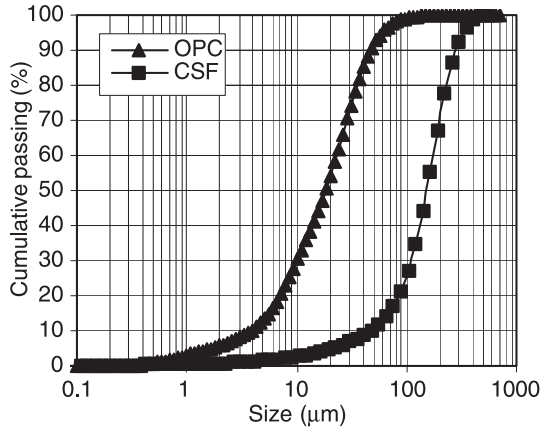

Fig. 1. Particle size distribution of cement and silica fume by laser diffraction.

2.4. Pore structure

The pore structures of CSF0, CSF5, CSF10, CSF15 and CSF20 were measured by mercury intrusion porosimetry (MIP). After reaching the prefixed curing ages, the middle portion of the samples was taken and broken to small pieces of dimension about 4–6 mm, then immersed in acetone to extract the free water, and further dried in a vacuum desiccator. The samples were evacuated to 50 μm Hg and the low pressure was generated up to 30 psi by nitrogen gas to gradually force the mercury into the pores on the surface of the sample. The penetrometer was then installed in high-pressure port to perform high-pressure analysis. The pressure was subsequently increased to a maximum pressure of about 60,000 psi. The relationship between pressure at equilibrium and pore size can be presented by the Washburn equation [7].

2.5. Compressive strength

The compressive strength of silica fume blended cement paste and the control sample was tested at related curing ages. The loads were applied to the samples with a rate of 100 kN/min.

3. Results and discussion

3.1. SEM test results and discussion

The particle characteristics of silica fume and morphologies of hydration products were viewed by SEM. The silica

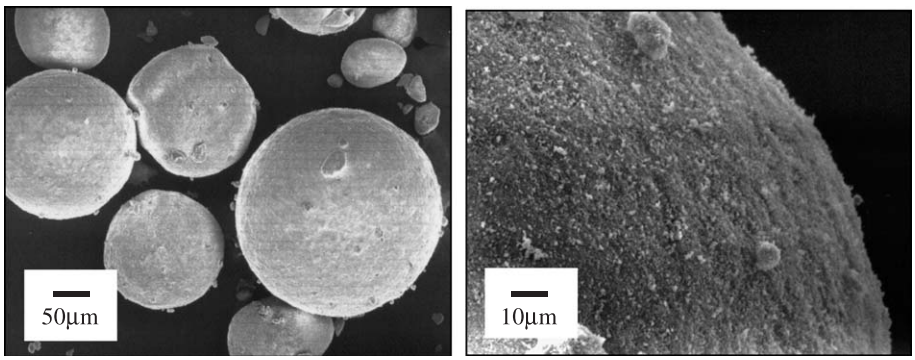

Fig. 2. Particle morphologies of silica fume by SEM. (a) Shape and size of silica fume. (b) Silica fume agglomeration.

fume agglomerations are almost spherical as shown in Fig. 2(a). The agglomeration consists of many ultra-fine silica fume as presented by Fig. 2(b). Some agglomerations have sizes larger than 100 μm. It agrees with the laser diffraction test results as shown in Fig. 1. It can be deduced that the SEM and laser diffraction measured the size of silica fume agglomeration, while the BET can measure all the particles' surface even if they are agglomerated as nitrogen molar is small enough to penetrate into the space inside silica fume agglomeration.

These agglomerations were very difficult to be dispersed to its original extreme fine size as 0.2 μm by some physical or chemical treatments such as strong mixing, adding a superplasticizer or treating by a supersonic homogenizer [5,6]. The difficulty of redispersion was showed by some investigators as the coarse agglomerations were found in hardened cement paste [4–6,8,9]. In Nagataki et al.'s [5] test results, about 70% of silica fume particles are larger than 10 μm after being treated by a ball mill, and more than 40% were larger than 10 μm after being treated by a supersonic homogenizer. Bye [3] pointed out that the pelletized silica fume is suitable for milling with Portland clinker in a cement mill. Granules may be broken down and dispersed in a concrete mixer by the aggregate. Aged agglomerated aqueous suspensions may need to be redispersed before use.

The large agglomerations were found existing in all samples in our experiment for curing ages from 3 to 90 days, with silica fume replacement from 5% to 20%. Fig. 3 is the SEM test result of CSF15 at 90 days age, which shows that silica fume agglomerations were not satisfactorily dispersed. Most of them reserve the original shape and size as in Fig. 2. Some researchers have proven that the pozzolanic reaction can only take place from the surface of the agglomeration [6,8]. Bonen and Diamond [8] found an unreacted core within a siliceous particle up to 1-year of age by backscatter SEM. The Ca/Si mole ratios have been determined by EDXA from the surface to the center of silica fume agglomeration and this ratio was found to be zero in the core. Mitchell et al. [6] discovered that the C-S-H was present on the outer surface of silica fume and intact silica fume was present within the core of the agglomeration.

It can be deduced from previous research work that the pozzolanic reaction starts from the surface of silica fume and the reaction front was penetrated into particle gradually by diffusion-controlled reaction [6,16]. The coarse silica fume agglomerations reduce significantly the effective sur-

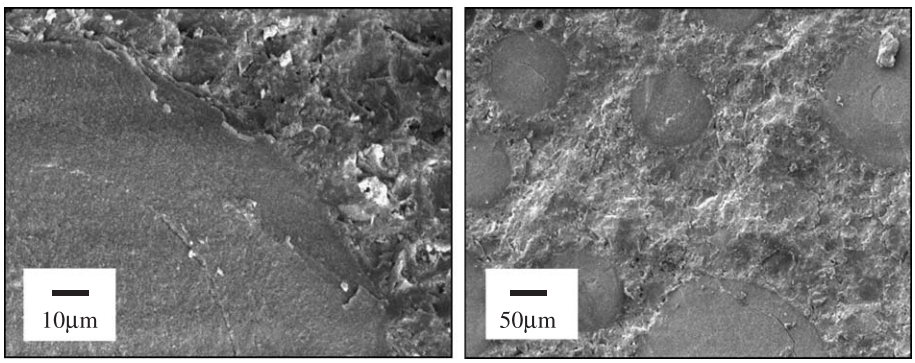

Fig. 3. Silica fume agglomeration in blended cement paste CSF15 at 90 days age, which reserve the shape and size of silica fume raw material.

face area for contacting and reacting with $Ca(OH)_2$, which definitely cut down the rate of pozzolanic reaction of silica fume. It is the particle size of silica fume agglomeration that determines the reactivity of silica fume rather than the original extreme fine silica fume.

3.2. MIP test results and discussion

The pore size distribution curves measured by MIP of CSF0, CSF5, CSF10, CSF15 and CSF20 are presented in Fig. 4(a)–(e). These results were further analyzed and presented in Table 2. The total porosity was divided into porosity P_1 (with pore size larger than 10 nm, which is defined as capillary porosity) [3] and porosity P_2 (with pore size from 3 to 10 nm, which is partly of gel porosity) according to the pore size distribution curves. It can be seen from Table 2 that the total porosity and capillary porosity P_1 were decreasing with the curing age for any mix proportion as expected. The total porosity of five mix proportions measured by MIP ranges from 37.36% to 22.61% from 3 to 90 days curing ages. At the same curing age, the differences or variations found of total porosity in different silica fume replacement are not significant. However, it can be noticed from Table 2

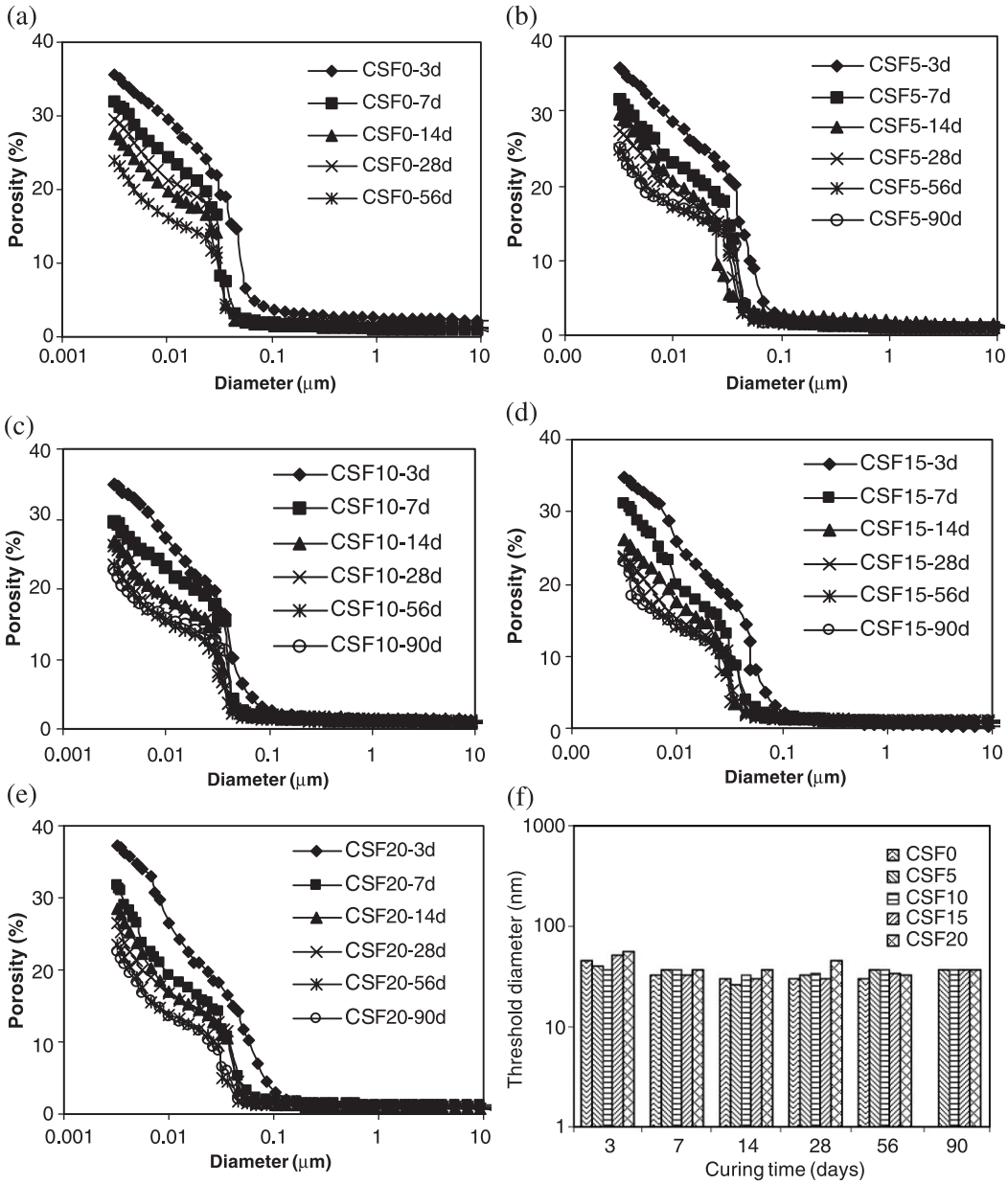

Fig. 4. (a–e) Cumulative pore size distribution curves by MIP. (f) Threshold diameters.

that their pore size distributions are different. The capillary porosity decreased with the increase of silica fume replacement. At higher silica fume content, there is a lower capillary porosity.

The pore size corresponding to the highest rate of mercury intrusion per change in pressure is known as the threshold diameter [10]. The threshold diameter may provide a good indicator of material durability as it has an important influence on the permeability and diffusion characteristics of the cement paste [11]. The threshold diameter results are presented in Fig. 4(f). There is no reduction of threshold diameter caused by silica fume replacement for all the curing ages and mix proportions, while some previous reports showed obvious reduction of threshold diameters by silica fume replacement [13,14].

It is generally accepted that the silica fume improves pore structure in two ways: its small particle size results in a filler effect in which the silica fume particles bridge the spaces between cement grains and the spaces between cement grains and aggregate; and the silica fume reacts pozzolanically with calcium hydroxide to produce a greater solid volume of C-S-H gel, leading to an additional reduction in capillary porosity during hydration [12]. The filler effect seems impossible, as the silica fume agglomeration size is much coarser than the cement particle. Even after treatments like supersonic homogenizer, ball mill or superplasticizer, the particle size of silica fume is in the same order as OPC particles [5]. In addition, the coarse silica fume agglomerations reduce significantly the effective surface area for contacting and reacting with $Ca(OH)_2$, which definitely affect the pozzolanic reactivity of silica fume. The nonsufficient pozzolanic reaction caused by the coarse agglomerations cannot improve the pore structure significantly.

Table 2
Pore structure measured by MIP

Curing time (days)	CSF0	CSF5	CSF10	CSF15	CSF20
Total porosity measured by MIP (%)					
3	35.69	35.72	34.90	34.74	37.36
7	31.97	31.54	29.69	31.16	31.77
14	27.62	29.55	26.79	26.06	28.39
28	26.90	27.36	26.31	23.82	26.39
56	23.95	24.90	23.57	23.64	23.56
90	–[a]	25.00	22.69	22.96	22.61
P_1 (%), $d>10$ nm					
3	29.52	28.68	27.29	25.90	26.41
7	24.44	23.12	23.09	19.91	19.36
14	19.82	20.59	18.86	17.45	16.97
28	19.38	19.27	18.26	15.06	16.68
56	16.08	17.26	15.38	14.19	13.77
90	–	17.50	15.88	14.02	13.54
P_2 (%), 3 nm$<d<$ 10 nm					
3	6.17	7.04	7.61	8.84	10.95
7	7.53	8.42	6.60	11.25	12.41
14	7.80	8.96	7.93	8.61	11.42
28	7.52	8.09	8.05	8.76	9.71
56	7.87	7.64	8.19	9.45	9.79
90	–	7.50	6.81	8.94	9.07

[a] Pore structure of CSF0 at 90 days was not measured by MIP.

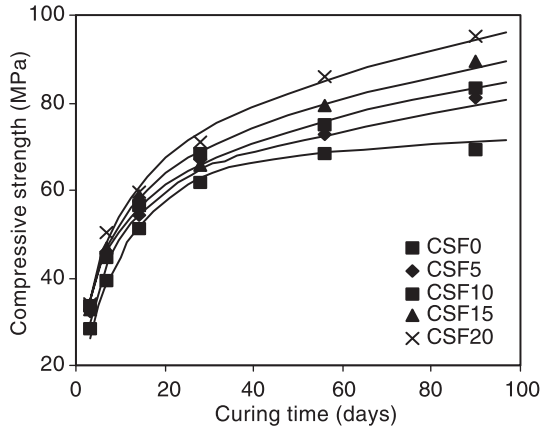

Fig. 5. Compressive strength of OPC and silica fume blended cement pastes.

3.3. Compressive strength test results and discussion

The compressive strength results are shown in Fig. 5. The compressive strength of five mix proportions all increase with curing age. The effect of silica fume on compressive strength at early ages was not significant, even up to 28 days. It became obvious at late ages (i.e. 56 and 90 days). Coarse silica fume agglomeration results in nonefficient improvement on compressive strength. The size of agglomerated silica fume controls the properties of blended cement pastes. The potential pozzolanic reactivity may probably be reduced by coarse silica fume agglomeration. They cannot react with $Ca(OH)_2$ completely even at 90 days of curing age. This slow pozzolanic reaction results in low strength increment up to 28 days.

4. Conclusions

(1) The silica fume agglomeration has been found in blended pastes, which cannot be broken down by normal mixing. The compressive strength of blended cement paste is not significantly increased up to 28 days due to this agglomeration.
(2) Pore structure is not sufficiently refined by silica fume replacement. The threshold diameter, which is an important parameter on permeability, is not reduced by silica fume replacement comparing with the control sample at the same curing age, although capillary porosity is reduced by several percentages.
(3) A total dispersion of densified silica fume in pastes must be carried out in order to get the maximum performances of blended matrixes.

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